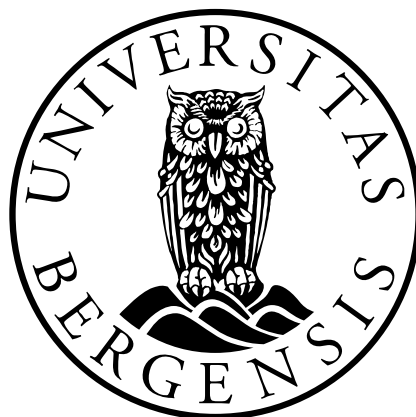# Physico-Chemistry Characterization of Sulfonated Polyacrylamide Polymers for Use in Polymer Flooding

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Preface

This thesis submitted for the degree Philosophiae Doctor (PhD). PhD project has been performed at Centre for Integrated Petroleum Research (CIPR), department of Chemistry, University of Bergen in the period from August 2006 to August 2009. The work was a part of PETROMAKS project "Enhanced oil recovery (EOR) for maximizing tail production", which included studies of displacement mechanism for polymer flooding, surfactant flooding, microbial enhanced oil recovery (MEOR), foam injection , and water alternative gas (WAG) processes. The work has been financed by the Norwegian Research Council and the industry partner Total E&P, Norway and Total E&P, France.

The main task in this thesis is to study sulfonated polyacrylamide polymers with a range of different sulfonation degree and molecular weight. The purpose was to build up knowledge about the rheological properties and adsorption/retention of studied polymers for high salinity and high temperature applications.

This dissertation comprises two parts:

Part one (introduction): This part consists of general information regarding to the physico-chemistry characterization of sulfonated polyacrylamide polymers, and states the objectives of this research. It starts with a general overview about polymer applications in oil industry, and followed by the viscosity and adsorption/retention study of polymers which must be well known before the application processes. Here all the main properties of the studied polymers will be discussed and after wards in the next part the results will be presented in different scientific papers.

Part two (Papers): This part is consisted of three scientific papers; first one which is "Viscosity Study of the Salt Tolerant Polymers" Journal of applied polymer science, Vol 117(3), pp 1551-1157. Second paper is about the adsorption and retention of the studied polymers, has been proceeding of 15th European symposium on improved oil recovery,

Paris, France, April 2009, and the third one which contains information about the viscosity and retention of the studied polymers at high temperature recently has been submitted to the journal of applied polymer science and reviewed in April 2010.

Acknowledgements

Abstract

Hydrolyzed polyacrylamide polymer (HPAM) as a feasible and effective viscosifier has been fully studied and used for polymer flooding processes in several oil field, e.g. Daqing oil field. It has been shown that Hydrolyzed polyacrylamide polymers (HPAM) may be a good choice for high temperature condition with no oxygen and no divalent ions presence. At high temperature and high salinity conditions, polymer may precipitates and loss their viscosyfing properties. Also adsorption and retention of polymer in porous medium may change rheological properties of polymers. Thus, the viscosyfing property of polymers is influenced by several important parameters, e.g. salinity, hardness, temperature, adsorption, retention, polymer structure, and etc.

By replacing some of carboxylate group of HPAM with another monomer, e.g. sodium salt of acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMPS), effect of high salinity/hardness and temperature seems to be reduced specially for the samples with higher percentage of AMPS co-monomer.

The ultimate aim of this work is to develop an understanding of the sulfonated polyacrylamide copolymers with a range of different sulfonation and molecular weight at high salinity and high temperature conditions. Most of the work in this thesis deals with viscosity and adsorption/retention measurements of the sulfonated copolymers and HPAM.

The factors which may affect the viscosity of the polymers and have been identified in this work as most likely influencing also adsorption and retention of the polymers are shear rate, polymer concentration, sulfonation degree, molecular weight, NaCl concentration, divalent ion concentration, and temperature.

List of papers

Paper 1

"*Viscosity Study of Salt Tolerant Polymers*", Rashidi, M., Blokhus, A. M. and Skauge, A. Journal of Applied Polymer Science, Volume 117, Issue 3, Pages 1551-1557.

Paper 2

"*Static and Dynamic Adsorption of Salt Tolerant Polymers*", Rashidi. M., Blokhus, A. M., and Skauge, A. Proceedings of 15th European symposium on improved oil recovery, Paris, France, April 2009.

Paper 3

"*Viscosity and Retention of Sulfonated Polyacrylamide Polymers at High Temperature*", Rashidi, M., Blokhus A. M., and Skauge, A. Journal of Applied Polymer Science, Reviewed by April 2010.

Nomenclature and Greek letters

A   Area of contact of the layers, Eq. 2.1

C   Polymer concentration (ppm)

C^* Critical overlap concentration (ppm), Eq. 2.7

C_i Molar concentration of ith ion, Eq. 3.2

F   Fractional force, Eq. 2.1

I   Ionic strength, Eq. 3.2

K_{rw} Relative permeability to water, Eq.1.1

K_{ro} Relative permeability to oil, Eq.1.1

M   Mobility ratio, Eq. 1.1

m   Total number of polymer macromolecules, Eq. 2.8

n   Fraction of carboxyl residue, Eq. 2.8

S_o Residual oil saturation

T   Temperature (^{o}C)

Z_i Charge of the ith ion, Eq. 3.2

γ Shear rate (s^{-1}), Eq. 2.2

μ Viscosity (mPa.s), Eq. 2.1

η_r Relative viscosity, Eq.2.3

η_s Solvent viscosity(mPa.s), Eq.2.3

η_{sp} Specific viscosity, Eq.2.4

η_R Reduced viscosity(ppm^{-1}), Eq.2.5

$[\eta]$ Intrinsic viscosity (ppm^{-1}), Eq.2.6

μ_o	Oil viscosity in porous medium (mPa.s), Eq.1.1
μ_w	Water viscosity in porous medium (mPa.s), Eq.1.1
τ	Degree of hydrolysis (%), Eq.2.8
σ	Shear stress(Pa),Eq.2.2
Γ	Adsorption density (mg/g)
Γ_s	Surface excess quantity, Eq. 3.1

Abbreviations

AMPS	Sodium salt of acrylic acid and 2-acrylamido-2-methyl prepane sulfonic acid
EOR	Enhanced oil recovery
HPAM	Hydrolyzed polyacrylamide
IBA	Isobutyl alcohol (isobutanol)
IPA	Isopropyl alcohol (isopropanol)
mD	milli Darcy
MD	Million Dalton
Mw	Molecular weight (MD)
PAM	Polyacrylamide
ppm	Part per million
PV	Pore volume
S/L	Solid/liquid ratio
SSW	Synthetic seawater
UV	Ultraviolet

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Chapter 1

Introduction

Oil production has three different stages; primary (production by natural reservoir energy), secondary (on the supply of external energy into the reservoir in the form of injecting fluids to increase reservoir pressure) and tertiary production (enhanced oil recovery methods increase the mobility of the oil in order to increase production). Over the lifetime of the oil field the pressure will fall, and at some point there will be insufficient underground pressure to lift the oil to the surface. In order to maintain the reservoir pressure, and sweep out oil in a more efficient way, water flooding as secondary oil production is a practical and effective way for many reservoir formations. A problem with water flooding is that in many cases oil has higher viscosity than water, and this however may lead to an unstable displacement. Increasing the viscosity of injected water by adding a polymer will improve sweep during water flooding process. It is necessary to study and evaluate the rheological properties of the polymers before implementation as polymer flooding (Sorbie, 1991).

The fundamental understanding of water flooding and the principle of strengths and weaknesses of the method goes back to the 1950s. To solve the problem of unstable displacement during water flooding, polymer was suggested in the early 1960s.

Polymers either biopolymers or synthetic polymers have several types of applications. Some of these applications are for oilfield, e.g. profile modification, drilling, and chemical flooding (Needham and Doe, 1987).

In polymer flooding process, a water soluble polymer either biopolymers or synthetic is added to injected water. Water/oil mobility ratio is the only mechanism to describe why using polymer can make water flooding more efficient. Both mobility ratio and its effect on diverting water from the swept zones to unswept zones will be described below.

Mechanism description based on mobility ratio: In water flooding processes independent on heterogeneity, oil can not be swept uniformly. Mobility ratio is a key factor for areal sweep which defined for water flooding process as (Craig 1980):

$$M = \frac{k_{rw}(S_{or})\mu_0}{\mu_w k_{ro}(S_{wi})} \tag{1.1}$$

Where; k_{rw} is relative permeability to water, k_{ro} is relative permeability to oil, μ_o and μ_w are oil and water viscosity respectively. As eq. 1.1 shows, if M increases then recovered oil before water breaks through decreases. Added polymer will improve the mobility ratio both by increasing μ_w and in some cases by decreasing k_{rw}, therefore there will be a potential to recover more oil especially for the reservoirs with high unswept oil.

The effect of mobility ratio on diversion effect: The effect of polymer on improving areal sweep efficiency is more effective in homogeneous reservoirs, but true homogenous reservoirs rarely exist. Reservoirs contain heterogeneity in both areal and vertical profile. All these heterogeneities lead water entry into more permeable zones, and considerable part of the reservoir, low permeable zones, remains unswept. Injected polymer will build up flow resistance in the portions of the reservoir that are swept by flooded water, through the permeability reduction or viscosity increase which have been discussed earlier. This increased resistance will subsequently divert the injected water to the unswept or poorly swept areas, so that the oil trapped in that zone can be efficiently recovered (Needham and Doe, 1987).

Polymer used in oil production: Hydrolyzed polyacrylamide (HPAM) polymer which is partially hydrolyzed form of polyacrylamide (PAM) established as a mobility control agent with potential to improve water flooding process, described by Pye and Sandiford (1964), and Gogarty (1967). Both biopolymers, e.g. Xanthan, and synthetic polymer, e.g. HPAM, have been used for actual polymer flooding processes. Several polymer flooding projects have been carried out successfully, both technically and economically (Han, et al. 2006; and Dong, et al. 2008).

Even though HPAM and Xanthan have been used for polymer flooding processes, they have specific limitations. For example HPAM has well known limitations at high temperature more than 70°C, and high salinity reservoirs with total dissolved solids (TDS) more than 40000 ppm (Moradi-Araghi et. al, 1987). Proceeding of amide group hydrolyses to form carboxylate group which is more severe at temperature higher than 70°C, and in the presence of divalent ions, will result in polymer precipitation, and then reduce brine viscosity. The strong binding between the divalent ions and carboxylate group in HPAM, results in the polymer molecules to precipitate more and this will decrease the viscosyfing property of HPAM polymers.

Recently, Seright et. al, (2009) have shown that HPAM still can be used in enhanced oil recovery processes at elevated temperature, e.g. 120°C, with no oxygen and divalent ions present. To obtain such a oxygen free condition there may be some proposed ideas; first to use recycled produced water to make polymer solutions, because the most reservoirs environment are reducing environments and produced water is almost oxygen free. Second, during the polymer flooding process surface facilities must be regularly controlled to prevent oxygen leakage development. Sometimes oxygen scavengers and antioxidants also may be used (Shupe 1981; Wellington 1983). All these concerns show that oxidation is an important mechanism which may affect polymer solution stability in terms of viscosity at elevated temperatures.

In the other side the effect of dissolved oxygen on polymer solution viscosity by itself is not critical (Muller 1981). However oxygen with many other substances, e.g. metals (especially ferrous iron), free radicals generating chemicals (like potassium persulfate), high or low pH and etc, caused substantial chemical degradation of polyacrylamide polymers (Knight 1973; Shupe 1981; Muller 1981).

Xanthan also has been used in classical polymer flooding. In contrast to HPAM, Xanthan gum is a rigid double helix polysaccharide which is not easily shear degraded, and also is more salt and divalent ions tolerable. However, the main problems of using biopolymers are biodegradation and injectivity problems (Moorhouse et. al, 1977; Seright and Henrici 1990; and Ryles 1988).

The other specific limitation which may change polymer rheological properties is adsorption and retention. The physical interaction (electrostatic attraction and van der Waal's dipole-dipole interaction (Baijal, 1981)) between the polymers molecules and the solid surface of porous medium will result in the adsorption of some polymer molecules on the rock surface. In addition to the adsorption there is also some mechanical entrapment of the polymer macromolecules in some of the narrow pore throat in porous medium.

The retention which is a general term and defined as the summation of adsorption and mechanical entrapment is a common problem of all polymers in porous medium. Loss of polymer due to retention causes lower viscosity of fluid. High adsorption level on the rock surface, and tendency to shear degradation at high flow rate also are also some other disadvantages of HPAM (Zaitoun and Potie 1983; and Ryles 1988).

To meet requirement in high temperature and high salinity reservoirs with synthetic polymers, the structure of HPAM has to be modified. Several modifications have been introduced, e.g. hydrophobically associating polymers, different copolymers of

polyacrylamide with anionic and cationic co-monomers, etc. Some of these modifications are to replace carboxylate group in HPAM with another monomers, e.g. sodium salt of acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMPS).

The specific objectives of this research project are to:

- To measure the rheological properties of PAMS and HPAM solutions, such as: steady-shear viscosity and viscosity behavior as functions of shear rate; polymer concentration; salinity, including divalent ion effects; polymer molecular weight; sulfonation degree; temperature; anti oxidant concentration.

- To measure transport of various PAMS and HPAM solutions in sandstones, in terms of adsorption and inaccessible pore volume with different process variables: sulfonation degree, polymer molecular weight, and salinity. This is done with a series of laboratory core flood experiments.

Three scientific papers have been extracted from this work and in the papers different results of the sulfonated polyacrylamide polymers properties have been elaborated. The first paper, discuss results of the viscosity study of the studied polymers. The effect of shear rate, salt, hardness and polymer concentration, at ambient temperature on the viscosity stability has been presented. In the second paper, results of the static adsorption and dynamics retention at ambient temperature have been discussed. The third paper includes the stability in terms of viscosity, of the studied polymers exposed for 1 year at $80^{o}C$. The dynamic retention of these polymers at $80^{o}C$ also was tested.

Chapter 2

Polymer Properties

This chapter will shortly introduce several main polymer properties. Viscosity of polymer solutions and the effect of some parameters, e.g. temperature, shear rate, divalent ($MgCl_2$, $CaCl_2$) and monovalent ($NaCl$) ions on the polymer solution viscosity will be discussed.

2.1   Polymer structure

A polymer is composed of many simple, repeating structural units of similar or different type of molecules which called monomers. A polymer may consist of hundreds to a millions of these repeating units with three different structures which are; linear, branched and network as shown in Figure 2.1.

Linear polymer

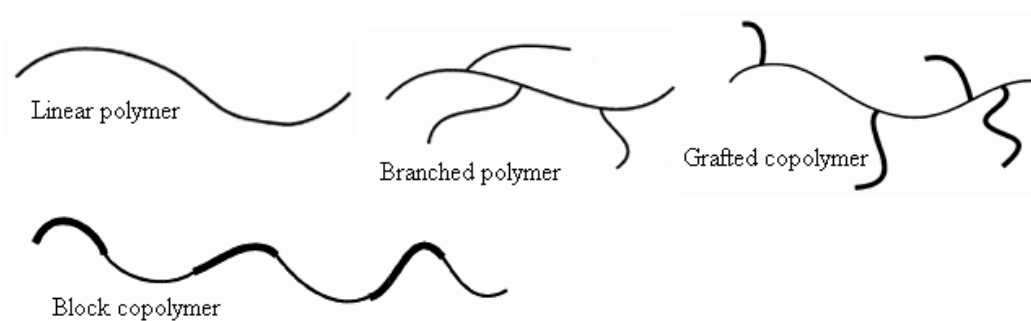Branched polymer

Grafted copolymer

Block copolymer

Figure 2.1. General schematic of different polymer structures

For example hydrophobically associative polyacrylamide polymers are a kind of grafted copolymers and contain a small or large amount of hydrophobic group which has been

linked directly to the polymer molecule structure. In aqueous solution hydrophobic group of these polymer tends to associate together to minimize their exposure to the aqueous solution. This is some how similar to the micelle formation of a surface active agents (surfactant) above its critical micellar concentration, and as a result of this association, solution viscosity increases (Taylor and Nasr-El-Din 1995; Shulz et. al, 1987; Lacik and Selb 1995; Candau et. al, 1996; Uemura et. al, 1995).

2.2   Polyelectrolyte

Polyelectrolyte is a group of polymers which may have one or several electrolyte groups in their repeating unit (monomer). HPAM and sulfonated polyacrylamide polymers are polyelectrolyte and simply anionic, i.e. they have negative charges on the carboxylate group and sulfonic acid group respectively, and this make polymers water soluble,(Fig. 2.2 A and B).

A)   B)
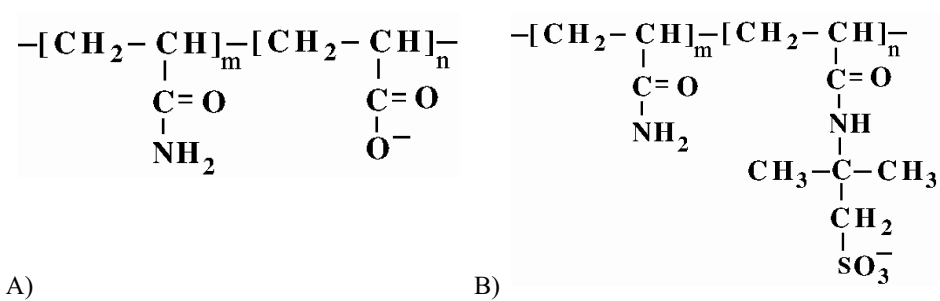
Figure 2.2. Molecular structure A) HPAM, and B) sulfonated polyacrylamide polymers

The polyelectrolyte properties are similar to both electrolyte and polymer solutions (Bueche 1962; Baeurle and Nogovitsin, 2007). In water solvent they have the same property as other polymers, but in aqueous solvent their electrolyte groups surrounded by the solvent counter ions. The effect of counter ions on the polyelectrolyte solution will create some limitation for their viscosyfing properties.

HPAM as a polyelectrolyte, develop high viscosity in fresh water, because its molecules are very flexible, this property is known as random coil in polymer chemistry (Sorbie, 1990). Since HPAM molecules are more flexible, then it makes them more sensitive to salt ions compare to other studied polyelectrolyte, e.g. sulfonated polyacrylamide polymers.

HPAM like other polyelectrolyte solutions in the presence of salt ions will react and coil up after a certain amount of salt concentration. As showed in Figure 2.2(B), the sulfonated polyacrylamide polymers also belong to polyelectrolyte which contains a small hydrophobic group with a length of only 1 Carbon atom. This short chain hydrophobic group may affect the viscosyfing properties of these polymers especially for the polymer with the lowest sulfonation degree, e.g. 5 mole %, which is more hydrophobic than the other sulfonated polymers. All the studied polymers in this work with their characteristics are given in Table 2.1.

Table 2.1. Polymers characteristics

Polymer*	Molecular weight (Million Dalton)	Sulfonation degree (Mole %)
AN105	6	5
AN113	8	13
AN125VLM	2	25
AN125	8	25
AN125VHM	12	25
AN132	8	32
HPAM	8	-

*For all the studied polymers information about their molecular weight and sulfonation degree was supplied by the manufacturer, and they have not been verified. In the following part the effect of some parameters on the polyelectrolyte behavior will be discussed.

2.3   Fluid flow behaviour of polymer solution

The term rheology is defined as the study of the deformation and flow of different fluids in response to surface forces (stress) (Bird, et al., 1960). The mathematical relationship between stress and deformation rate (strain rate) is constitutive equation. The Newtonian relationship between stress and strain rate is the simplest example of a rheological constitutive equation as:

$$F = \mu A \frac{dV}{dx}$$

(2.1)

Where; F is force which apply on the surface of the fluid, A is the contact area between two adjacent layers in the fluid, $\frac{dV}{dx}$ is the velocity gradient between the two layer, and µ which is a proportionality constant, is simply called fluid viscosity (Bird et. al, 1960).

The fluid viscosity is simply defined as the fluid resistance to shear (Bird, et al., 1960). Based on this simple definition it is possible to formulate fluid viscosity as:

$$\sigma = \mu \gamma$$

(2.2)

Which σ (Pa) is shear stress which implies on the fluid surface, µ (Pa.s) is fluid viscosity and γ (s^{-1}) is shear rate.

Generally as showed in equation 2.2, fluid may be classified as Newtonian or non-Newtonian fluids. The viscosity of Newtonian fluids, e.g. water, is constant and it is not a function of shear rate. Polymer solution generally classified as non-Newtonian fluids, i.e. the viscosity changes with shear rate and it is not constant. This change in the viscosity as

a function of shear rate is different for different fluids as presented in Figure 2.3 (Bird, et al., 1960).
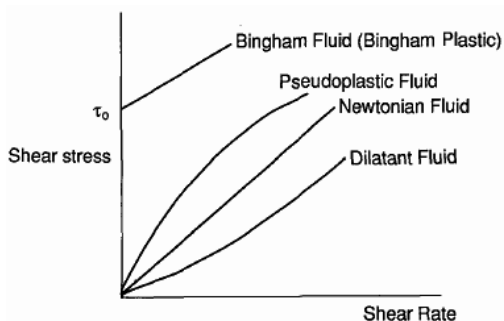
Figure 2.3. Different type of fluids (classified based shear stress /shear rate relationship)

In pseudo plastic fluids, known also as shear thinning, the viscosity deceases as shear rate increases, and vast majority of polymer solutions are shear thinning in their nature. Shear rate is not the only factor which can affect the viscosity of polymer solution, but there are several other parameters which may affect polymer viscosity behaviour, e.g. molecular weight, polymer concentration, and the nature of polymer and solvent. The target of this work is to evaluate the effect of all these parameters on the viscosity of studied polymers.

2.4   Effect of polymer concentration and molecular weight on the viscosity

For all polymers, higher the polymer molecular weight and concentrations gives a solution with higher viscosity. This is because the polymer concentration changes the interactions among polymer molecules, and the molecular weight directly affects the chain size. While polymer with higher molecular weight gives a solution with higher viscosity, however they are easily shear degradable (mechanical degradation). For example HPAM with high molecular weight is an effective viscosyfing polymer, but it is easily shear degradable.

To relate viscosity to the polymer concentration and molecular weight there are some other viscosity quantities, e.g. relative viscosity, specific viscosity, reduced viscosity which the definitions of these viscosity quantities are (Billmeyer, 1971; Rodriguez, 1983):

Relative viscosity (η_r): is the ratio of the viscosity of a solution (η) to the viscosity of the solvent used (η_s)

$$\eta_r = \frac{\eta}{\eta_s} \tag{2.3}$$

Specific viscosity (η_{sp}): which is the relative viscosity of a polymer solution with a known concentration minus 1, and usually determined at low polymer concentration

$$\eta_{sp} = \eta_r - 1 \tag{2.4}$$

Reduced viscosity (η_R): The ratio of the specific viscosity to the polymer solution concentration

$$\eta_R = \frac{\eta_{sp}}{C} \tag{2.5}$$

C is polymer concentration (here, unit used for polymer concentration is ppm). Specific viscosity expresses the incremental viscosity due to the presence of the polymer in the solution. Reduced viscosity is a measure of the specific capacity of the polymer to increase the relative viscosity, also known as viscosity number. Since the solution used for viscosity measurements will be non-ideal, i.e. the behavior is not predictable over a

wide range of concentrations and temperatures by the use of Raoult's law, therefore reduced viscosity will depend on polymer concentration. It will be useful to extrapolate reduced viscosity to zero concentration. The extrapolated reduced viscosity to zero is known as intrinsic viscosity, [η], and will be defined as:

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C} \qquad\qquad (2.6)$$

In which $[\eta]$ is a property related to the polymer molecular size and polymer chain extension in solution. The dimension of intrinsic viscosity is reciprocal of the concentration dimension, ppm^{-1}(Huggins 1942).

Polymer solution for different polymer concentrations can be divided into three regimes; dilute(C< C*), transition (C=C*), and semi-dilute or concentrated (C>C*) regimes. C* which is critical overlap concentration at dilute regime can be calculated by using intrinsic viscosity as defined below (Gupta et al. 2005):

$$C^* = \frac{1}{[\eta]} \qquad\qquad (2.7)$$

In this work intrinsic viscosity was used to calculate critical overlap concentrations (C*) in dilute regimes.

2.5   Effect of ions and pH on the viscosity

To understand the effect of ions, monovalent and divalent, on the viscosity behavior of the polyelectrolyte solutions, the interaction of these ions with the charges on the polymer chain must be understood.

Molecules of polyelectrolyte in distilled water may be almost fully expanded due to the repulsion between the similar charged groups distributed along the polymer chain. In aqueous solvents because of positive mobile ions, the charges on the polymer chain are screened and degree of expansion decreases. Some theories also have been implemented to explain the effect of salt ions on the rheological behavior of polyelectrolyte solutions (Tanford, 1961; Flory, 1953).

Here, salt ions divide into two categories; monovalent ions, e.g. Na^+ or K^+ and divalent ions, e.g. Ca^{2+} or Mg^{2+}. HPAM molecules are more sensitive to divalent ions compare to monovalent ions. It has been generally accepted this is due to the strong binding between divalent ions and carboxylate group (COO^-) (Lipton, 1974; Sandvik and Maerker, 1977; Szabo 1979; Zaitoun and Potie, 1983; Moradi et al., 1995; Martin and Calgon, 1995). After a certain divalent ions concentration HPAM will precipitate and this make HPAM unfavorable for EOR processes for high salinity/hardness condition (Figure 2.4). It must be mentioned, Temperature is another significant cause of viscosity reduction which it will be discussed later.
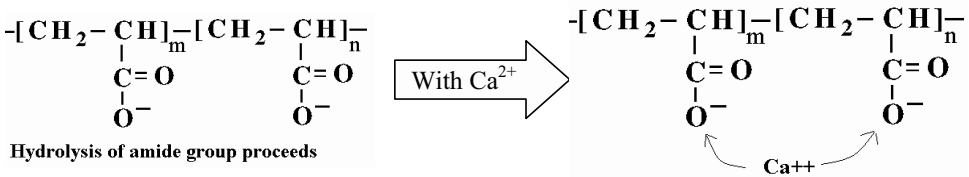

Figure 2.4 Schematic of polymer precipitation with the presence of divalent ions

The negatively charged carboxyl or AMPS groups in high pH conditions induce extension of the molecules through electrostatic repulsion among the groups, thereby increasing viscosity; conversely, low pH conditions cause the molecules to become coiled, resulting in low-viscosity Mungan (1969).

2.6 Degradation processes and its effect on the viscosity

Degradation refers to any processes which may break down polymer molecular structures. Therefore, to use polymers in enhanced oil recovery processes their properties must be stable and degradation must be prevented. Viscosity as the main polymer property may be degraded either chemically, mechanically or biologically (Sorbie 1980). Below a short description of each will be discussed:

Mechanical degradation (also known as shear degradation): Mechanical degradation is short term degradation refer to the polymer molecular structure break down due to high shear rate and mechanical forces close to the wellbore. Noik and Audibert (1994) studied the mechanical degradation of one sulfonated polyacrylamide with 25 mole % sulfonation degree and HPAM. As results showed sulfonated polyacrylamide polymers due to the rigidity of sulfonate group have better resistance to mechanical degradation.

Biological degradation: This refers to the microbial break down of the polymer molecular structure. Mostly this degradation mechanism may be considered for biopolymers. For synthetic polymers this type of degradation is not considerable.

Chemical degradation: Break down of polymer macromolecular structure either short term, e.g. by oxidation in the presence of oxygen or long term, e.g. by hydrolysis and precipitation mechanisms. In this work, chemical degradation is the only degradation process which has been considered and mainly discussed during the project.

2.7 Polymer oxidation prevention mechanisms

Oxygen is one of the well known chemical species which critically can impact the viscosity of polymer either HPAM or sulfonated co-polymers. As mentioned in the introduction, HPAM is more efficient viscosifier at anaerobic condition (with no oxygen present), and without divalent ions present.

HPAM is most commonly used for polymer flooding applications due to its low cost and good viscosyfing ability. Further, it has a molecular structure that allows for better injectivity into porous media too much effort has been to find a way to minimize the effect of divalent ions at high temperature on the viscosity of HPAM.

One proposed idea was to make HPAM solutions at fresh water and then inject it into a reservoir with hard saline brine. Even though saline formation brine mix with the polymer solution and lower the polymer viscosity. But the injected polymer bank maintains its integrity during oil displacement in a reservoir with hard saline brine (Maitin 1992). Pope et. al, (1978) and Lake (1989) experiment results showed that, due to ion exchanges and reservoir rock properties divalent ions may release, therefore to avoid HPAM precipitation these concepts also must be well understood and controlled. For example one proposed idea to control this released divalent ions from clay minerals is to inject a solution with a fixed ratio of monovalent to divalent ions in the reservoir (Lake, 1989). Also to maintain low divalent ions concentrations limit, it requires injecting low salinity water. With all above mentioned ideas HPAM still at high temperature with divalent ions present is unfavourable for EOR (polymer flooding) applications.

2.8   Effect of antioxidants, reducing agents on the stability of the viscosity

Alcohols can prevent oxidization of the polymer; because the alcohol can be easily oxidized and thereby as sacrificial agent protect the polymer against oxidization (Shupe 1981; Wellington 1983; Ryles 1983). In this work Iso-Butyl-Alcohol (IBA) has been used.

There are some other chemicals which may have the same effect as alcohol, e.g. thiourea, sodium hydrosulphite, formaldehyde, biocids and surfactants. For example formaldehyde may increase the polymer stability in terms of viscosity, but it depends on the source of formaldehyde preparation. The results of Shupe's (1981) study on three different

formaldehyde samples showed that, a mixture of formaldehyde and methanol will be more effective than only formaldehyde. Also the mixture with higher formaldehyde

percentage was more effective in order to prevent oxidization of polymer, and the effect of formaldehyde alone also was better than the effect of methanol alone.

The optimum concentration of formaldehyde in order to have a better effect on the stability of the viscosity was tested and it was in the range of 200 to 400 ppm.

Thiourea as another chemical with a great effect on the polymer stability in terms of viscosity of polyacrylamide polymers has been tested (Schurs and McKennon, 1996). To optimize the results of using thiourea on the stability of the viscosity, concentration has an important role. Higher the concentration gives better stability results in terms of viscosity. The mixture of thiourea and other chemicals, e.g. IPA, can be more effective than the use of thiourea alone. For example a mixture of thiourea with a concentration of 400 ppm, and IPA with a concentration of 800 ppm, is more efficient to prevent polymer oxidation and viscosity losses. It must be mentioned, unlike the formaldehyde which may be considered as a biocide, by using thiourea as an antioxidant additional biocids is also required in order to control bacterial growth and prevent biological degradation.

2.9   Polymer hydrolysis and precipitation mechanisms

At high temperature and high salinity concentrations, proceeding of the amide group hydrolysis makes these polymers unfavourable (Parker and Lezzi 1993). Degree of hydrolysis (τ) defines as the fraction of the carboxyl residue (n) replacing acrylamide units (m) over the total number of the polymer macromolecule.

As shown in Figure 2.2 (A), the degree of hydrolysis is defined as:

$$\tau = \frac{n}{n+m} \qquad\qquad (2.8)$$

Degree of hydrolysis is important and can affect the physical properties of the polymers, e.g. polymer rheological properties (Davison and Mentzer, 1980), solution viscosity, polymer retention, flow resistance properties (Martin and Sherwood, 1975), and fluid flow behaviour (Lewandowska, 2006).

It should be mentioned that for the sulfonated co-polymers in addition to the hydrolysis of amide groups, the AMPS co-monomer group also may hydrolyse at temperature higher than 100^oC and pH 8 (Audibert, Argillier, 1995; Parker and Lezzi 1993). If pH decreases then the rate of hydrolysis will increase. For example at pH 6, the rate of hydrolysis is 5 times faster than pH 8, and this is due to the net negative charge on the polymer which is higher at pH 8. Therefore direct affect of hydroxide ions on amide group is more difficult because of greater electrostatic repulsion (Parker and Lezzi 1993). Introducing AMPS co-monomer group into the polyacrylamide polymer molecular structure showed raise in the stability limit in terms of viscosity of polyacrylamide at least up to 120^oC. But for reservoir with temperature more than 120^oC, AMPS co-monomers can not protect acrylamide against thermal hydrolysis (Moradi-Araghi et. al, 1987; Audibert, Argillier 1995).

It is good to know that Taylor and Nasr-El-Din (1994) generally reviewed all methods for the determination of degree of hydrolysis. These methods are mainly by using titration methods, e.g. coductometric (Dexter and Ryles, 1989), potentiometric (Jacovic and Zivojin 1973; Muller et. al, 1979) colloidal, spectroscopy methods, e.g. C^{13} Nuclear Magnetic Resonance (Gillet and Delpuech, 1980), infrared (Muller et. al, 1979), and Ultraviolet (UV) spectroscopy (Muller et. al, 1979). Here potentiometric titration was used to measure degree of hydrolysis.

Chapter 3

Polymer Adsorption and Retention Mechanisms

One of the most important properties which made polymer interested for EOR processes as mentioned earlier was their viscosyfing property. Another important parameter which may affect the feasibility study plan of a polymer flooding project is the retention and adsorption of polymer in porous medium. Adsorption and retention may be defined as the interaction between the polymer molecules and the porous medium which leads polymer to be retained or adsorbed (Sorbie, 1991). The adsorption and retention of polymer will affect both, polymer and porous medium properties. For example the viscosity of adsorbed polymer will be lower than the viscosity of the injected polymer. In the following sections more information of adsorption and retention will be presented.

3.1   Polymer adsorption/retention mechanisms in porous media

Polymer adsorption is mainly physical interaction, e.g. electrostatic attraction due to the charges differences between the solid surface and polymer or Van der Waal's dipole-dipole interactions. Polymer retention is more general, and consists of three main mechanisms; polymer adsorption, mechanical entrapment and hydrodynamic retention as shown in Figure 3.1 (Sorbie, 1991).
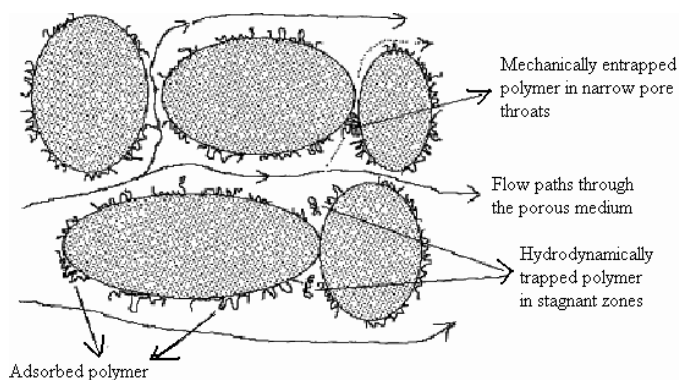
Figure 3.1. General schematic of different polymer retention mechanisms in porous medium

Adsorption mechanism which is the major part of retention will be discussed more afterwards, but mechanical entrapment happens when the polymer macromolecules trapped in narrow pore throat (Willhite and Dominguez, 1977). The hydrodynamic retention is not fully understood, but it was observed by the changes of polymer flow rate (Chauveteau and Kohler, 1974, Dominguez and Willhite, 1977).

3.1.1 Polymer adsorption and adsorption isotherms

In static adsorption measurements, the mineral sample is soaked in the polymer solution. The difference of polymer concentrations before and after mixing with rock sample is measured. The static adsorption onto the mineral surfaces is measured by the depletion method. The unit of retention level (Γ) is the mass of the polymer per unit mass of solid either in g/g or in µg/g. It is more scientific to measure surface excess (Γs) which is the mass of polymer per unit surface area of the solid. It should be mentioned that the solid surface is measured by gas adsorption using BET method (Gregg and Sing, 1982). Based on the above mentioned information for static adsorption measurement, the surface excess (Γs), [mass/area], can be calculated as:

$$\Gamma s = V \frac{(C_2 - C_1)}{A} \qquad\qquad (3.1)$$

Where; V is the volume of polymer solution with a known concentration of C_1, the measured concentration of polymer after being adsorbed is C_2, and A is the total surface area of the adsorbent. In this research silica specific surface area was 3.65 m^2g^{-1}, and kaolinite specific surface area was approximately 10.6 m^2g^{-1}, which were given by the supplier.

Adsorption is the only mechanism which remove polymer from the solution and results in a significant viscosity reduction at high level of adsorption. Typically, the adsorption by bulk static method is much larger than that by dynamic flow conditions (Lakatos et al., 1979). The presence of inaccessible pore volume and smaller specific surface area in dynamic methods reduces the actual rock surface area that is exposed to the polymer solution during flow.

In the static adsorption measurement flocculation of the mineral particles by polymer bridging, is an important parameter which may affect the adsorption. The flocculation is a function of solid-liquid (S/L) ratio (Argillier et. al, 1996). By increasing S/L ratio for a polymer solution with known concentration, due to aggregation of mineral particles the available surface to the polymer decreases and then total adsorption decreases. In the other side, very low S/L ratio make it difficult to measure the adsorption amount accurately because of the small difference in initial and final concentration. Here based on the experiment results, an optimum S/L of 0.005 was chosen to get a compromise between accurate measurements and representative values for adsorption ratio.

A general graph of adsorption isotherms of polyacrylamide polymers onto the silica mineral surface is shown in Figure 3.2. In the classical adsorption isotherms, plateau region is corresponded to the saturation of the mineral surface by the polymer chains (Fig. 3.2).

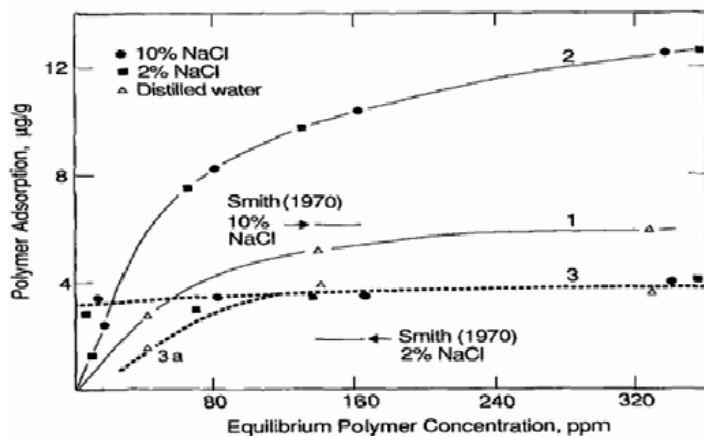Figure 3.2. Adsorption isotherm of HPAM onto the silica mineral surface (Szabo 1975)

In this work, for all studied polymers a classical type of adsorption isotherms was observed. The general conformation of adsorbed polymer molecules at a solid/liquid interface is shown in Figure 3.3.
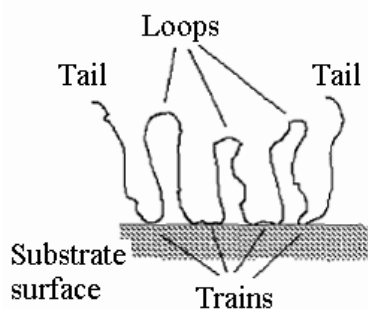

Figure 3.3. View of polymer molecules adsorption at a solid-liquid interface with tail, loops and trains (Sorbie, 1980).

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As shown in Fig. 3.3, the adsorbed layer of polymers on the mineral surface consists of trains, loops and tails.

3.1.2   Polymer retention

Retention of polymer as mentioned before is mostly consists of polymer adsorption. Some times it may involve mechanical entrapment of polymer macromolecules in porous medium, and to some extent hydrodynamically trapped polymer molecules in stagnant zones (Fig 3.1). The reason for the entrapment of polymer molecules in porous medium is simply due to the size of polymer molecules which may be larger than the size of pore throat. Retention experiments are simply the injection of polymer with a known concentration and a tracer into the core or sand pack. In this research to compare the result with adsorption experiments, Berea sandstone which is mainly consisted of quartz sand with about 4 % clay mostly kaolinite was used. Here, to perform retention experiments, 2 pore volumes (PV) of the polymer with tracer (100 ppm $LiNO_3$) solution was injected into the Berea sandstone core, followed by 3 pore volumes of the same the same salinity in order to wash out the polymer, while leaving the irreversibly-adsorbed polymer. Samples were collected in 4 ml intervals at the other end, and the polymer and tracer concentrations were measured. To measure the concentration of samples either in static or in dynamic experiments the starch triiodide method was used (Scoggins and Miller 1979). A complete material balance can then be obtained by calculating the difference between the mass of produced polymer and the amount of input polymer. By assuming that there is no viscous instability with chase-brine injection, because of the small core diameter (10 cm) and the relatively low polymer viscosity.

To measure the tracer concentration inductively coupled plasma atomic emission spectrometry (ICP-AES) was used. Polymer concentrations alterations were found to affect the measurement, higher polymer concentrations led to a lower measured lithium concentration. Probably the changes in viscosity and/or surface properties affect the sample introduction system so that less sample is introduced with polymer present.

To solve this, the effluent samples were diluted 100 times with a 1 wt. % HNO_3 solution, and an internal standard (1 ppm Yttrium) was used to correct the signal.

Figure 3.4 shows a general effluent production of injecting a known pore volume of polymer solution with tracer post flushed by a known pore volume of solvent. Here, for all studied polymers the same effluent profiles as Fig. 3.4 were observed.
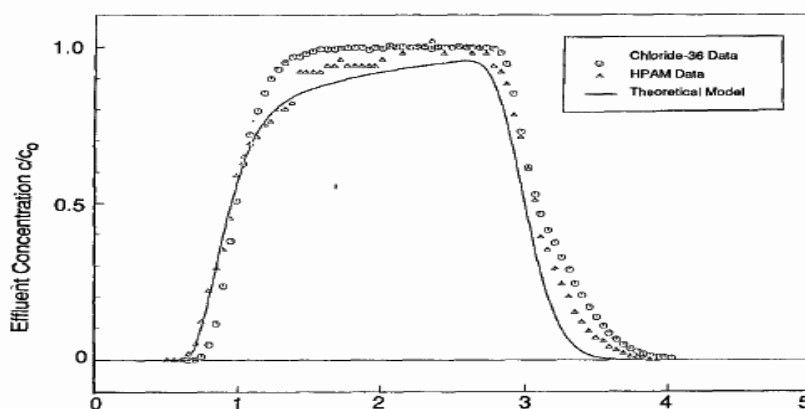

Figure 3.4. Experimental and modelled for effluent profile of injecting 2 PV of 50 ppm HPAM and ^{36}Cl tracer in sandstone cores (Sorbie et. al. 1989)

3.2   Main parameters governing adsorption and retention

Several parameters, e.g. solvent property, temperature, type of solid surface, polymer properties for example sulfonation degree and molecular weight can affect adsorption and retention. In this work, the effect of all mentioned parameters has been investigated and results have been discussed in paper 2.

3.2.1   Influence of solvent and solid properties on the adsorption

To study the effect of solvent on the adsorption two different solvents with the same ionic strength one with divalent ion and the other without divalent ions have been used. Ionic strength of the solvent measured as:

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$$I = \frac{1}{2} \sum_{i=1}^{n} \left(Z_i^2 C_i \right)$$
(3.2)

Where; Z_i is the charge of ith ion, C_i is its molar concentration of ith ion. Based on Eq. 3.2, ionic strength of synthetic seawater with NaCl (25000 ppm), KCl (700 ppm) and divalent ions, Ca^{2+} (1700 ppm), Mg^{2+} (11000 ppm), is equivalent to the ionic strength of 5 wt. % NaCl solvent. Based on the flocculation power of monovalent and divalent ions ($Na^+ = 1$, $K^+ = 1.8$, $Mg^{2+} = 27$, and $Ca^{2+} = 45$, Rengasamy and Summer 1998), in the adsorption test on kaolinite surface the effect of flocculation for the studied polymers in 5 wt. % NaCl was less pronounced than SSW (Lu et al. 2002; Rashidi, et al. 2009). The main reasons are; cations have more charge screening ability than monovalent, also divalent ions may be more effective to act as a binding ion between the anionic surface sites of the mineral and AMPS or Carboxylate group in sulfonated polyacrylamide polymer or HPAM respectively (O'Gorman and Kitchener, 1974).

As Figure 3.5 shows, in addition to ions, mineral soil texture also may affect the adsorption of polyacrylamide polymers.
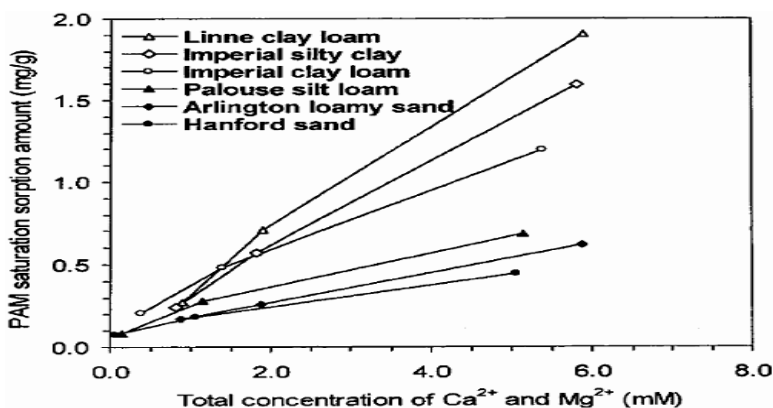

Figure 3.5. Influence of divalent ion concentrations for different soil texture on the polyacrylamide adsorption (Lu et al. 2002).

The same behaviour with slower trend compared to divalent ions is seen for monovalent and different soil textures, which is shown in Figure 3.6.
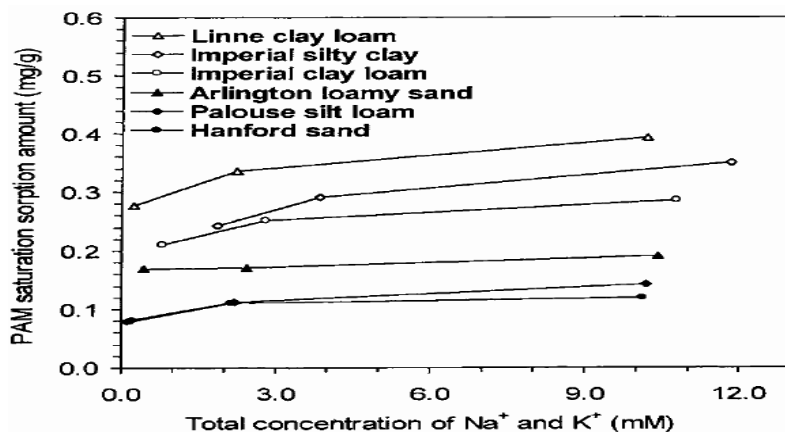
Figure 3.6. Influence of monovalent ion concentrations for different soil texture on the polyacrylamide adsorption (Lu et al. 2002).

3.2.2 Influence of inaccessible pore volume on the polymer retention

As mentioned before tracer is a chemical with almost no adsorption onto the mineral surface, and one important reason to inject tracer with polymer into the core is to better understand the principle of polymer transport behaviour in porous medium. One aspect of the effect of polymer molecular weight on the retention is due to the inaccessible pore volume, which is presented in Figure 3.7.
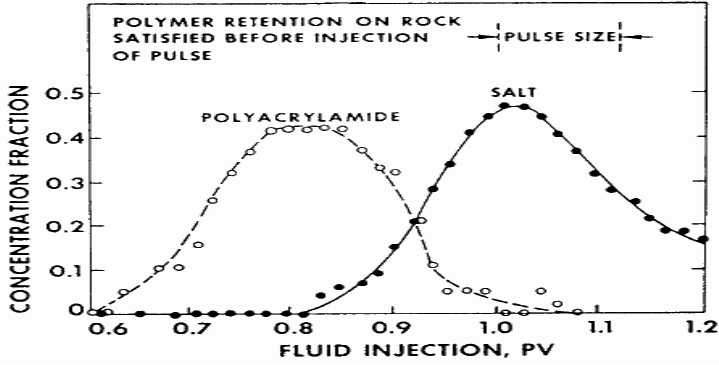
Figure 3.7. Effluent profiles of injected polymer and tracer (salt) with inaccessible pore volume (Dawson and Lantz, 1972).

As Fig. 3.7 shows, the tracer is produced later than the polymer, indicating that some of the pore volume is accessible to the tracer, but is inaccessible to the polymer macromolecules, similar polymer transport behaviour also was found by Lakatos and Lakatos-Szabo (1980). In the calculation and mathematical modeling of polymer flooding process this must be considered, and compensated.

Chapter 4

Main Results

4.1 Polymer characterization for EOR applications

The main objective in this project is related to investigate sulfonated polyacrylamide polymers for applications especially to high salinity and high temperature applications (Figure 4.1). The laboratory testing includes viscosity measurement at ambient and high temperature, adsorption/retention, and core tests.

Figure 4.1. Limitations of brine salinity (total dissolved solid, TDS) and reservoir temperature of conventional polymers and challenge for research and development.
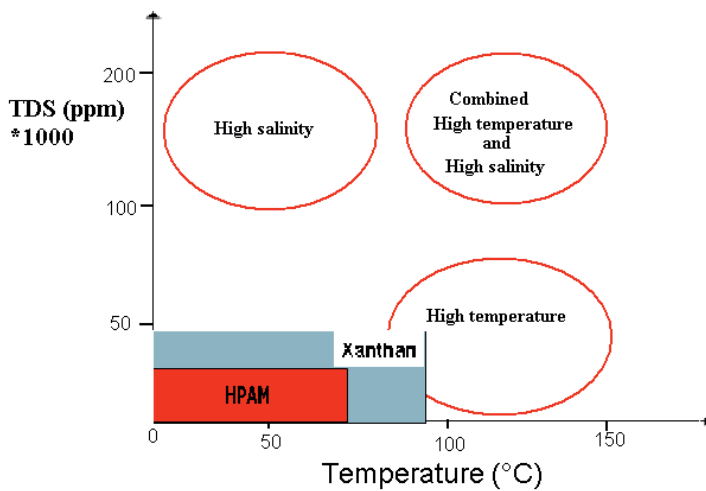
So far a systematic study of the sulfonated polyacrylamide polymers regarding to their viscosity behaviour both at ambient and elevated temperature, salt and hardness tolerance, adsorption and retention at ambient and elevated temperature, has not been performed. In this thesis main focus was on the investigation of the effect of sulfonation degree, molecular weight and IBA concentration variations on the viscosity behaviour of these polymers. In this respect a comparison was made among the out coming results of the sulfonated polyacrylamide polymers with HPAM with the same molecular weight as sulfonated polyacrylamide polymers, e.g. 8 MDalton. In this chapter a summary of the main results which have already been presented in papers 1 to 3 will be discussed.

4.2   Viscosity study of the polymers at ambient temperature

Main studied rheological property of the sulfonated polyacrylamide and HPAM was polymer solution viscosity. Study of the effect of several parameters, e.g. shear rate, polymer concentration, salt concentration, the presence of divalent ions, redissolution of precipitated polymer are presented in Paper 1.

Sulfonation degree may affect fluid flow behaviour and shear rate dependence of viscosity. At low polymer concentrations, e.g. less than 1000 ppm, the polymer solutions behave like Newtonian fluids i.e. the viscosity is shear-independent, within the range of shear rate studied. For higher polymer concentrations, however, the viscosity is found to decrease with shear rate as for pseudo-plastic (shear thinning) fluids (Paper 1). By increasing the sulfonation degree, shear rate dependence of viscosity decreases (Paper 1, Figure 3). This is due to the introduction of AMPS co-monomer unit in the hydrolyzed polyacrylamide molecular chain. AMPS co-monomer unit probably increase the rigidity of polymer molecule chain, and then will induce better resistant to shear (Ballard et. al, 1988).

As results show at a given NaCl-concentration, the critical overlap concentration, C*, is found to decrease as the sulfonation degree of the polymers increases (Table 3, Paper1).

This decrease can be explained by the increase in the charge density of the polymer chain resulting in more extended polymer molecules where fewer polymer molecules (or less concentration) are needed for interaction between the polymer chains.

The effect of salt concentration on the viscosity of studied polymer is shown in Figure 4.2.
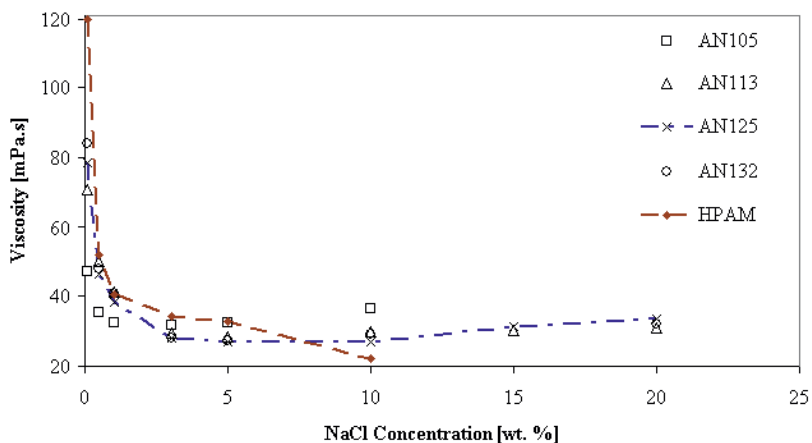
Figure 4.2. The viscosity of sulfonation polyacrylamide polymers, and HPAM with the same molecular weight, e.g. 8 MDalton, and different sulfonation degree, as a function of NaCl concentration, 5000 ppm polymer concentration, 100 s^{-1}, 20°C

As shown, generally for all polymers viscosity decreases as a function of salinity, this can be explained as screening of the charges on polymer chain by cations (Ait-Kadi, et. al, 1987; and Chegas, et. al, 2004). Further as shown in Figure 4.2, at low NaCl concentration, e.g. less than 1 wt. %, the polymer with the highest sulfonation degree has highest viscosity. For NaCl concentrations above 3 wt. %, the polymer with the lowest sulfonation degree gives the highest viscosity, as was explained in section 2.2, this behavior must likely is due to more hydrophobicity of the polymer with the lowest sulfonation degree (McCormick et. al, 1993; and Uhl et. al, 1995). Generally, when

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AMPS co-monomer is introduced, polymer stability in terms of viscosity increases and this make sulfonated copolymer favorable for more high salinity applications. Also as expected the viscosity increases with increasing molecular weight. For all sulfonated polyacrylamide polymers except the one with the lowest molecular weight (Figure 7, Paper 1) the viscosity at 10 wt. % NaCl concentration is higher than HPAM.

The effect of divalent ions on the viscosity losses of the studied polymers is also given in table 4.1.

Table 4.1. Viscosity (mPa.s) for 5000 ppm sulfonated polyacrylamide polymers and HPAM, in two solvents with the same salinity, e.g. synthetic sea water and 5 wt. % NaCl (Rashidi et. al, 2009) (Table IV, Paper 1).

Polymers	AN105	AN113	AN125	AN125VHM	AN132	HPAM
5 wt. % NaCl	32.6	28.6	27.1	34.2	27.4	33.5
Synthetic seawater	29.7	27.9	27.0	31.1	24.6	24.4

Compare to HPAM The effect of divalent ions on the viscosity losses is lower for sulfonated copolymers independent on sulfonation degree. As introduced in section 2.5, HPAM is more sensitive to divalent ions due to the strong binding between divalent ions and carboxylate group (COO^-) (Lipton, 1974; Sandvik and Maerker, 1977; Szabo 1979; Zaitoun and Potie, 1983; Moradi et al., 1995; Martin and Calgon, 1995).

As been discussed in section 2.5, in the presence of divalent ions especially Ca^{2+} more than a certain concentration, the polymer will precipitate and come out of the solution. The precipitation mechanism differs with NaCl present (Table V, Paper 1). Generally, solubility of HPAM in hard brine (with Ca^{2+}) by adding NaCl to the solution will improve (Schwartz and Francois 1981, Zaitoun and Potie 1983). The same result was observed for PAMS copolymers, and higher NaCl concentration (20 wt. %) increase solubility of polymer more than at lower NaCl concentration. It can be seen that solubility of PAMS copolymers in hard brine (with Ca^{2+} and 15 wt. % NaCl) will

increase with sulfonation degree. In all cases viscosity was better maintained with divalent ions present at high salinity concentrations for PAMS copolymers than HPAM.

4.3   Viscosity study of the polymers at 80°C

The influence of high temperature on the viscosity losses of the studied polymer was studied explicit and the results are presented in Paper 3. In this work, all test and measurements were performed under aerobic condition. These studied have been performed both, with and without added IBA, in which without IBA all the polymers more and less after 90 days loss their viscosity (Table III, Paper 3). It can be seen that an increase in IBA concentration (Figure 5, Paper 3), leads to increase polymer stability in terms of viscosity. In 5 wt. % NaCl solvent, stability of viscosity by adding IBA levels off at 3 wt. % IBA concentration, but the highest IBA concentration(5 wt. %) is the best choice for achieving a maximum solution viscosity in solvent with divalent ions present (Figure 5, Paper 3). For all presented results a fixed IBA as an optimum concentration, 3 wt. %, was chosen.

Figure 4.3 shows the results of the effect of sulfonation degree for studied polymers at ambient and exposed at 80°C for 90 days.
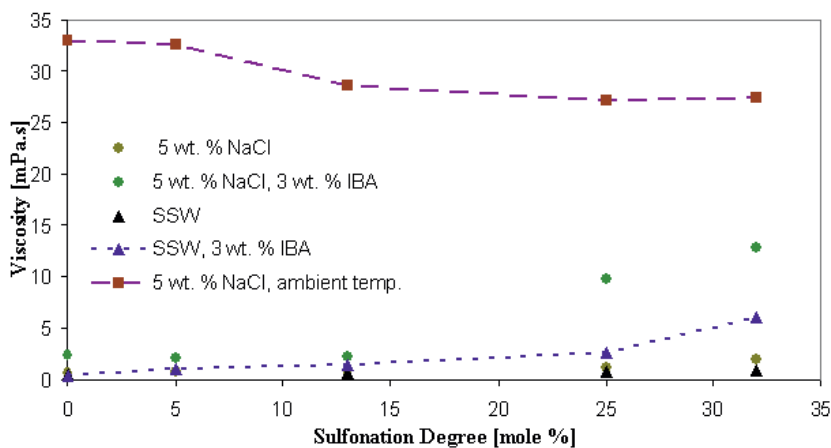
Figure 4.3. The viscosity as a function of sulfonation degree at ambient temperature(5000 ppm polymer concentration) and exposed 90 days at 80°C, for the polymers with the same molecular weight, e.g. 8 MD, with (3 wt. %) and without IBA, at SSW and 5 wt. % NaCl, and at 100 s^{-1}.

Figure 4.3, indicate that there is difference between the effect of sulfonation degree at ambient and 80°C, which may confirm the effect of temperature on the viscosity behavior of these polymer. As explained above at ambient temperature, the viscosity of polymer with lowest sulfonation degree is better maintained at high salt concentrations. The possible explanation was due to less charge density on polymer chain. While at high temperature high viscosity is achieved for the polymers with sulfonation degree more than 25 mole % in 5 wt. % NaCl solvent. As seen, with divalent ions present the difference in viscosity is not so big, but still we have an increase in viscosity particularly for the polymer with the highest sulfonation degree, AN132.

Increase in sulfonation degree at high temperature may impact the viscosity behavior and shear rate dependence of polymers. At 80°C, the viscosity of HPAM solution decreases abruptly as function of aging time, but for the sulfonated polyacrylamide polymer with

highest sulfonation degree, AN132, the viscosity is more and less independent of aging time within studied time scale (Figure 1, paper 3).

Also the viscosity behavior changes at high temperature from shear thinning, i.e. viscosity decreases when shear rate increases, to the Newtonian behavior, i.e. the viscosity is shear independent. For HPAM it only takes 10 days to induce this transition in viscosity behavior, while for AN125 it takes about 7 months before we observe viscosity behavior changes towards Newtonian behavior (Figures 3 and 4, Paper 1).

As introduced in section 2.5, polyacrylamide in hard brine will precipitate, and high temperature severe the effect of divalent ions on precipitation enhancement. In this work, at 3 wt. % IBA concentration, with divalent ions present, precipitation has been observed for HPAM after 3 months and similarly for the polymer with the lowest sulfonation degree (AN105) after 7 months at 80^oC. No precipitation has been observed for the other sulfonated co-polymers even after a year exposed to 80^oC in SSW. In 5 wt. % NaCl solvent, no precipitation was observed for all the sulfonated co-polymers, but HPAM was found to precipitate after 7 months. This means that precipitation is not a major cause for viscosity loss of PAMS co-polymers. Therefore the major reason for viscosity loss of PAMS co-polymers seems to be degree of hydrolysis. The degree of hydrolysis of the sulfonated copolymers is directly dependent on the sulfonation degree, and this is in line with the other author's results for sulfonated polyacrylamide polymers (Ryles, 1988; Dexter and Ryles, 1989). The results confirmed that if sulfonation degree increases then the rate of hydrolysis decreases and levels off (Table IV, paper 3).

Figure 4.4 shows the effect of molecular weight on the viscosity changes at ambient and exposed 90 days at 80^oC for both 5 wt. % NaCl and SSW solvents.
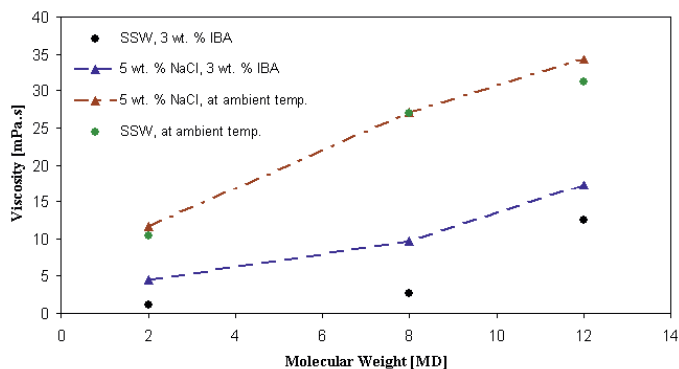
Figure 4.4. The viscosity as a function of molecular weight for the polymers with the same sulfonation degree, 25 mole%, exposed 90 days at 80°C and ambient temperature,[19] at 5 wt. % NaCl and SSW, and at 100 s^{-1} shear rate (Figure 7, Paper 3).

As shown in Fig. 4.4, the absolute value of the viscosity loss is higher for the polymer with higher molecular weight for both SSW and 5 wt. % NaCl with a larger effect at SSW solution.

4.4   Adsorption and retention of the studied polymers

4.4.1   Adsorption study results

The effect of main parameters on the adsorption and retention at ambient temperature was studied explicit and the results are presented in Paper 2. The effect of temperature on retention also was tested and results are given in paper 3.

As been introduced in chapter 3, in this work for static adsorption experiments two powdered minerals, e.g. kaolinite and silica were used. Kaolinite is a type of clay with negative overall charge and positive charge at the edges and silica has only negative surface charges. Due to repulsion between the charges on the silica surface and polymer chain the adsorption on the silica mineral surface was very low (Figure 3, Paper 2).

Generally for all the sulfonated polyacrylamide polymers the adsorption is considerably lower than HPAM. To avoid particle coagulation in the static adsorption experiments either at SSW or 5 wt. % NaCl solvents, different solid/liquid ratios were tested and at the end 0.005 has been chosen (section 3.1.1, and Figures 1 and 2, Paper 2).

The effect of sulfonation degree on the adsorption of polymers with the same molecular weight, 8 MDalton, and a range of sulfonation degree from 5 mole % to 32 mole % presented in Figure 4.5.
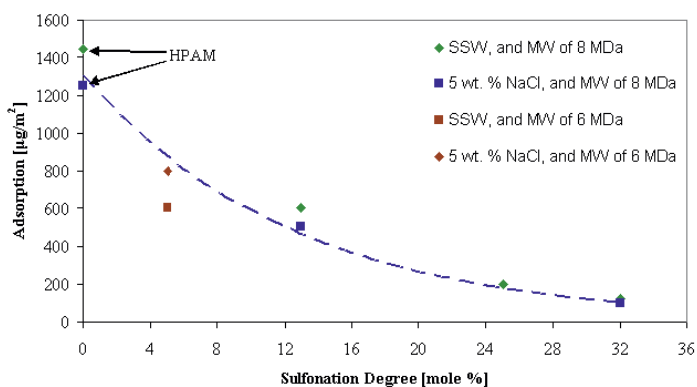
Figure 4.5. Adsorption of sulfonated polyacrylamide polymers, and HPAM on kaolinite as a function of sulfonation degree, S/L 0.005, 20°C (Figure 5, Paper 2).

As results show, the adsorption of the polymer with higher sulfonation degree was less than the other polymers. But due to the thickness of the adsorbed layer which is higher for the polymer with higher molecular weight (Hlady et al. 1982), the results showed that by increasing molecular weight the adsorption also increases (Figure 6, paper 2). This observation conforms to those of Lipatov et al. (1974) and Gramain et al. (1981). Gramain et al. (1981) interpreted that the polymers with higher molecular weight occupy a smaller fraction of segments anchored onto the surface, thereby leaving more areas for polymer adsorption. Other researchers (Lakatos et al., 1979; Lakatos et al., 1980) found a

higher adsorption level with increasing molecular weight of polymers, citing the reason of size contributions.

It is good to mention, for all calculations there were some sources of uncertainty both for polymer solution preparation and in concentration measurement. For this study the final amount of uncertainties is calculated using propagation of uncertainty (Figure 3, paper 2).

4.4.2 Retention study results at ambient temperature

Again as been discussed in chapter 3, retention at ambient and elevated temperature ($80^{o}C$), was investigated by injecting 3 pore volume (PV) of the polymer with a tracer followed by 2 PV post flush of solvent into the Berea sandstone cores. The dimensions of the used cores were around 10 cm long and 3.7cm in diameter. The permeability and porosity were around 500-700 mD, and 20% respectively.

As introduced in section 3.1, In addition to the adsorption which may be considered as the main retention mechanism of the studied polymers some other mechanisms, e.g. mechanical entrapment and constant shear rate of injecting polymer into the core also may affect the retention of these polymers.

To explain above mentioned mechanism as Figure 4.6 shows, the dynamic retention for the polymer with higher molecular weight (AN125VHM) was less than the polymer with lower molecular weight (AN125VLM). Interpretation of the effluent production profiles of the tracer with polymer solution into the core showed that the tracer, with no adsorption, came out after the AN125VHM (Fig. 4.7). This means that AN125VLM is behaving more and less like the tracer which has access to most of the pores in the core (Figure 4.8). While some of the pore volumes were accessible for tracer, at the same time were inaccessible for AN125VHM macromolecules (Lakatos and Lakatos-Szabo, 1980). Thereby it is deviated more from the tracer effluent production profile.
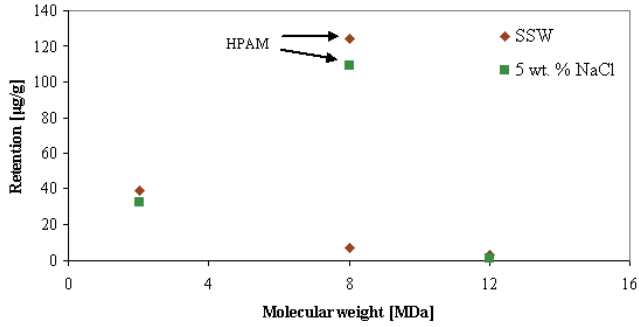
Figure 4.6. Retention of sulfonated polyacrylamide polymers with the same sulfonation degree (25 mole %), and HPAM as a function of molecular weight, on Berea, 20°C (Figure 9, Paper 2).

Figure 4.7. Example of effluent production from injection 2 PV of AN125VHM in SSW, 1000 ppm, retention on Berea at 20°C (Figure 7, Paper 2).

Figure 4.8. Example of effluent production from injection of 2 PV of AN125VLM in SSW, 1000 ppm, retention on Berea at 20°C (Figure 8, Paper 2).

As the effluent profiles for two polymers with the highest and lowest molecular weight in Figures 4.7 and 4.8 shows, possibly due to entrapment of high molecular weight polymer molecules in the porous medium, the retention for the polymer with higher molecular weight is lower.

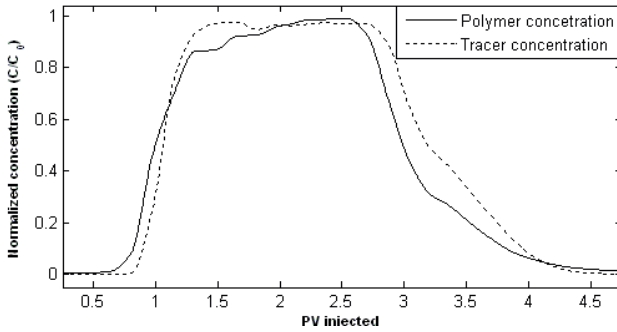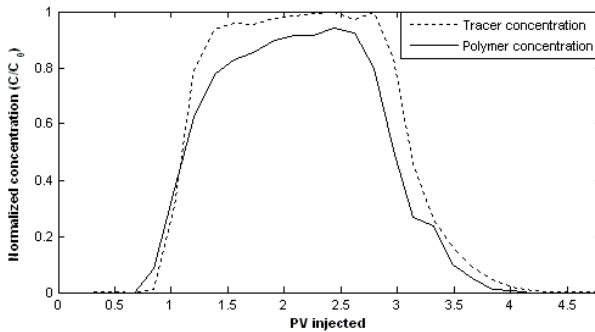The results of the sulfonation degree effect on the retention showed the same trend as it was for adsorption, this means that again the polymer with higher sulfonation degree is less retained in Berea sandstone cores (Figure 10, Paper 2).

4.4.3   Retention study results at 80°C

As results show in Paper 3, a small increase of the adsorbed amount of injected polymer at high temperature in comparison with the adsorbed amount of injection at ambient temperature was observed. This is also inline with the results of Noik et. al, (1994) study for one sulfonated polyacrylamide polymer with 25 mole % sulfonation degree at two different temperatures, 90°C and 100°C. As Noik et. al, (1994) showed he retention of the studied sulfonated polyacrylamide at the above mentioned temperature was the same. Then temperature can not be a remarkable challenge for the sulfonated polyacrylamide polymers as results shows in Table 4.2.

Table 4.2. The effect of temperature on retention of polymer in Berea Sandstone core at ambient and 80°C (Table V, Paper 3).

Retention (μg/g)						
Polymers	AN105	AN113	AN125VLM	AN125	AN125VHM	AN132	HPAM
SSW at 20°C	111.5	58.7	39.0	--	3.2	16.5	124.2
SSW at 80°C	111.7	59.9	46.8	--	10.5	19.9	139.0

4.5   Summary of main results

Different sulfonated polyacrylamide polymers have been investigated to determine whether high temperature, high salinity and hardness have a significant effect on the viscosity stability, and adsorption/retention of these polymers during enhanced oil

recovery processes. The influence of several parameters has been investigated. The tasks were investigated by the means of viscosity and adsorption/retention measurements with modified Anton-Paar viscometer and other used apparatuses.
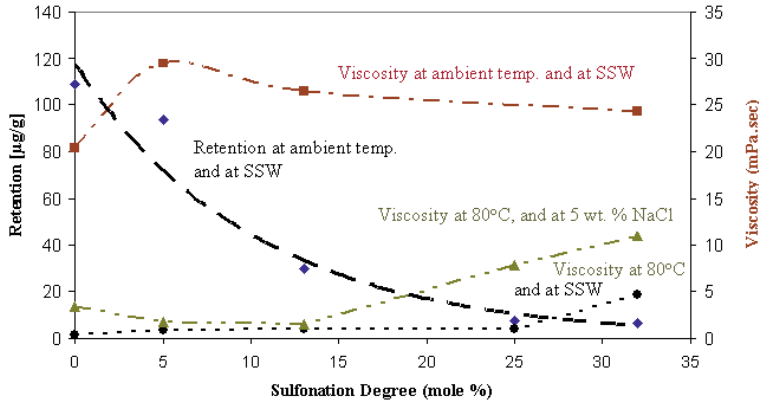
Figure 4.9. A general comparison between the sulfonated polyacrylamide polymers for their viscosity and retention in SSW and 5 wt. % NaCl, at ambient and 80°C.

As general results show (Figure 4.9), for the sulfonated polyacrylamide polymers only minor reduction in viscosity by increase in sulfonation degree, but there was a substantial decrease in retention and adsorption and also the polymer viscosity is better maintained both in 5 wt. % NaCl and SSW solvent at high temperature. The results showed that high sulfonation degree is more favourable and should be further investigated for polymer flooding in moderate high salinity and high temperature reservoirs. In addition to increase in sulfonation degree, increasing molecular weight can further improve the viscosity.

Chapter 5

Concluding Remarks and Future Work

5.1   Concluding remarks

The influence of temperature, salinity/hardness on the viscosity and adsorption/retention of sulfonated polyacrylamide during enhanced oil recovery was investigated. Several factors have been identified as an influence on the viscosity and adsorption/retention of the studied polymers. These factors are listed here according to their assumed importance:

1. **Viscosity:**

- Effect of shear rate and polymer concentration on viscosity:

At low polymer concentration (<1000 ppm) sulfonated copolymers behave Newtonian, while at higher concentration they are shear thinning. Replacing some carboxylate groups in HPAM with AMPS co-monomers increases rigidity of the polymer molecules. For sulfonated copolymers higher sulfonation degree is more shear thinning (shear rate 10-1000 s^{-1}). Increase in mole % of the sulfonation degree, which is equivalent to increase in charge density on polymer chain will; decrease critical overlap concentration (C*) for a specific salt concentration.

- Effect of ions on viscosity:

Sulfonated copolymers maintain viscosity from 1 wt. % NaCl up to 20 wt. % NaCl. At low salinity, e.g. less than 3 wt. % NaCl, the highest sulfonation degree gives highest viscosity, opposite trend was obtained at high salinity.

Generally, strong binding between divalent ions and –COO⁻ make HPAM molecules more sensitive to divalent ions. Replacing some of –COO⁻ with sulfonated group in a polyacrylamide chain makes it less sensitive to divalent ions. The sulfonated copolymers with highest sulfonation degree are more soluble in mixed brine (with Ca^{2+}) than the other sulfonated copolymers.

- Effect of temperature on viscosity:

Viscosity is maintained for test time up to 7 months at $80^{o}C$ for polymers with sulfonation degree of more than 25 mole % in 5 wt. % NaCl solvent and using 3 wt. % IBA. With divalent ions present, similar trend in viscosity with relation to sulfonation degree is observed.

The presence of the antioxidant, IBA, can increase the thermal stability, in terms of viscosity, of sulfonated polyacrylamide polymers. Good results were obtained with 3 and 5 wt. % IBA concentration in both 5 wt. % NaCl, and SSW solvents.

At high temperature the presence of divalent ions leads to strong reduction of HPAM solution viscosity, but the viscosity is better maintained for PAMS copolymer. Precipitation has been observed for HPAM which precipitated after almost 3 months, and also for PAMS copolymer with the lowest sulfonation degree (5 mole %) which precipitated after 7 months aging at $80^{o}C$.

2. Adsorption and retention

- Effect of sulfonation degree

Both adsorption and retention for the sulfonated polyacrylamide polymers are reduced with increasing sulfonation degree. Compared to HPAM a much lower retention is observed for the sulfonated co-polymers.

Retention was found to be relatively independent of temperature.

- Effect of molecular weight

Static adsorption increases for polymer with higher molecular weight.

The retention for polymer with higher molecular weight is lower due to inaccessible pores for larger molecules. Like all other polymers increasing molecular weight can further improve the viscosity of PAMS co-polymers.

Overall conclusion

The results of the viscosity stability and the desorption/retention of PAMS copolymer at high temperature, high salinity and hardness concentrations show, this group of polymers should be considered as an alternative to HPAM in more saline brine and at high temperature mobility control EOR processes.

5.2   Suggestions for future study

Some suggestions could be given for further work and they are as listed below:

First of all since our purpose was to test the polymers under aerobic condition, then at this stage further experiment at high temperature under anaerobic condition, to measure and control dissolved oxygen at each time step, can be suggested. This can be done by a

closed loop capillary viscometer. By this method two major problems will be prevented; first, the amount of dissolved oxygen and polymer oxidation is more under controlled, second, also evaporation of polymer solution at higher temperature during the viscosity measurement can be prevented.

At this stage it is good to study the viscosity of the polymer solutions even at higher temperature, e.g. more than 100°C for the polymer with higher sulfonation degree.

Another suggestion is to study the viscosity of some other polymers with the structure based on these sulfonated polyacrylamide polymers. For example, it could be useful to study a polymer with high sulfonation degree with increases molecular weight. Also to find out a sulfonated polyacrylamide polymer with more hydrophobic group, better solubility and better maintained viscosity at high temperature and high salinity.

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